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14. ABSTRACT Report developed under STTR contract for topic AF06-T023 This AF STTR Phase I work was aimed at developing spray coating methods and new coating materials for corrosion protection. Plasma and cold spray coating methods were selected. The explored coating materials were crystalline materials [AA 1100 for 2024-T3 & Al-2 Wt % Zn alloy for 7075-T6] and aluminum based bulk metallic glass (BMG) precursor materials [Al-5Fe-5Gd & Al-8Ni-5Y (atom %)]. Crystalline coating materials were cold sprayed onto substrate coupons at ASB Industries, Barberton, Ohio. Plasma spraying of crystalline and BMG materials was done at FIU, Miami, FL. The evaluations of the coated coupons include tensile tests and corrosion tests. The results are summarized below.  The corrosion responses of cold sprayed and plasma sprayed substrates with crystalline coatings were similar to original alclad materials. There is, however, some strength loss (up to 20%) of the substrate. An attempt to synthesize aluminum-based glassy coatings by plasma spray was not successful. Their SWAAT life is poor. There was very significant softening (up to 60%) in the BMG coated coupons. The development of glassy coatings is limited by non-availability of aluminum based BMG powder feedstock for spraying.					
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**CONTRACT No. FA9550-06-C-0113**

Contract Line Item No. 0001AC; Performance period: 1 Sept. 2006-31 May 2007

**Title: Development of spray coating methods and materials to replace aluminum cladding of aging aircraft for corrosion protection****ABSTRACT**

The objective of this AF STTR Phase I work was to develop spray coating methods and new coating materials for corrosion protection of aging aircraft. The requirements are that the coatings should be easily depot applied and also the temperature of the skin should not exceed 150°C during the process. This is to preserve the original temper of the substrate. Plasma spray and cold spray coating methods were selected for this study. The process parameters of the coating methods were optimized to meet the above requirements. The explored coating materials consist of crystalline materials [AA 1100 for 2024-T3 & Al-2 Wt % Zn alloy for 7075-T6] and aluminum based bulk metallic glass (BMG) precursor materials [Al-5Fe-5Gd & Al-8Ni-5Y (atom %)]. Crystalline coating materials were cold sprayed onto substrate coupons at ASB Industries, Barberton, Ohio. Plasma spraying of crystalline and BMG materials was done at FIU, Miami, FL. The evaluations of the coated coupons include microstructural characterization, tensile tests and corrosion tests. The results are summarized below.

The corrosion response, as indicated by corrosion potentials and SWAAT corrosion life, of coupons with cold spray coatings is similar to the original alclad for corrosion protection. There is, however, some strength loss (up to 20%) of the skin. The overall results of plasma sprayed specimens with crystalline coatings are similar to cold sprayed coatings. Even though, the coupon temperature did not exceed 100°C during plasma spraying, there was softening up to ~ 20 %.

An attempt to synthesize aluminum-based glassy coating by plasma spray was not successful in this study. Corrosion potentials indicate that the trial coatings of this study are cathodic to substrate and their SWAAT life is poor. There was very significant softening (up to 60%) in the BMG coated coupons. The development of glassy coatings is limited by non-availability of aluminum based BMG powder feedstock for spraying. The synthesis of glassy phase in the coating and softening of the substrate during spraying are the issues to be addressed in further work.

## I. PROJECT OBJECTIVES

Aging aircraft within the US Air Force have a severe corrosion problem. As the military fleet of aircraft ages, with many planes currently in excess of 20 to 25 years of service, the economic burden of maintenance and flight safety becomes prohibitive. It is desirable and advantageous to extend the life of aging aircraft by using an appropriate protective barrier coating that will prevent corrosion of the aircraft skin involving aluminum alloys such as AA 2024-T3 and 7075-T6. Historically, the method of corrosion protection of the aircraft skin has been through cladding of a suitable aluminum alloy onto the base alloy. The protective clad layer is applied through roll bonding prior to the final heat treatment of the skin material during the original manufacture of the air frame. While this method of roll bonding is applicable to the fabrication of new air frames, it is not suited for repairs of corroded layers of claddings for the obvious reason that the cladding is to be replaced without removing the skin of the aircraft. Currently, there are no suitable techniques for the application of cladding in this manner. Among materials for corrosion protection, recently published results suggest that amorphous alloy coatings have a high potential for corrosion protection. The objectives of this project are to develop deposition processes and new cladding materials for corrosion protection of aging aircraft. The cladding system should be easily depot applied. Another requirement of the clad application method is that the temperature of the substrate (skin) should not exceed 150°C during the process. Any further increase in temperature can damage the temper of the skin materials leading to their softening,

The proposed work was to develop both spray coating methods that can be easily depot applied and materials (crystalline and bulk metallic glassy alloys) that provide corrosion protection (galvanic and barrier). Plasma and cold spray methods were proposed for this study.

Technical objectives of Phase I work are as follows:

- Selection of conventional and amorphous aluminum alloys with a better promise for corrosion protection.
- Development of an appropriate type of spray coating method to deposit a suitable alloy (crystalline and amorphous) coating on the aircraft skin for corrosion protection. An important requirement of the spray coating method is that the substrate temperature should not exceed 150°C during the process. The thermal spray coating method needs to be optimized to meet the above requirements.
- Evaluation of the corrosion response of substrate coupons with different coatings using accelerated corrosion tests and corrosion potential measurements.
- Identification of the optimal processing method and coating material for best corrosion protection.
- Demonstration of the feasibility of Phase I approach.

## II. WORK PERFORMED

The following work was performed towards pursuing the objectives of this project.

### II-1. Coating Materials

#### II.1.1. Crystalline coatings

For protection against galvanic corrosion, it is well known that the coating material should be anodic to the substrate. Corrosion potential difference of  $\sim 20$  mV or more is desirable between the sacrificial anodic material and the substrate for this purpose. Among the crystalline coating materials, pure aluminum and Al-2 Wt % Zn alloy are well suited for 2024-T3 and 7075-T6 substrates, respectively. Accordingly, the following coating materials are selected for this study.

Crystalline coating materials: (i) AA 1100 for 2024-T3 substrate & Al-2 Wt % Zn alloy for 7075-T6 substrate. As it was not possible to procure Al-2 Wt % Zn powder from a commercial vendor, aluminum and zinc powders (in desired proportions) were blended in a ball mill for this purpose.

#### II.1.2. Bulk Metallic Glass (BMG) coatings

With increasing understanding of metallic glass, a variety of new-generation corrosion-resistant amorphous alloys have attracted considerable attention, such as Al-Ta, Al-Nb, Al-Ti, Al-Zr and Al-Cr. Several aluminum-transition metal alloys exhibit single amorphous phase in wide composition ranges. Fig.1 shows a comparison of the corrosion rate of the various aluminum alloys with those of conventional corrosion-resistant alloys measured in 1M HCl at 30 °C. The results indicate that when aluminum is alloyed with refractory elements, the alloys exhibit high corrosion resistance. X-ray photoelectron spectroscopic (XPS) analysis revealed that passive films are formed on Al-based amorphous alloys composed of cations of both aluminum and corrosion-resistant elements. Although aluminum oxyhydroxide is easily dissolved in acids, the formation of a double oxyhydroxide of aluminum and refractory metals provides high corrosion resistance.

Recently, research on Al-based amorphous alloys has been focused on Al-EM-LM and Al-R-LM ( EM = early transition metal, LM = late transition metal, R = rare earth metal) ternary alloys without metalloid because higher GFA (glass-formation ability) and better mechanical strength. It is worth to note that the amorphous phase of Al-based glasses has been shown to be stable for up to 2 years at room temperature, although such alloys tend to crystallize if heated with sufficient thermal energy to accelerate the kinetics of crystallization, nucleation and growth. The promising developments in Al-based amorphous alloys spur the materials scientists to apply these metallic glasses into practical corrosion-resistant applications. Sweitzer et al studied the corrosion resistance to micrometer-scale pit formation of  $\text{Al}_{90}\text{Fe}_5\text{Gd}_5$  and  $\text{Al}_{87}\text{Ni}_{8.7}\text{Y}_{4.3}$  alloys, the results indicated that the amorphous structure of the as-solidified Al-Fe-Gd and Al-Ni-Y alloys

significantly enhances repassivation potential ( $E_{rp}$ ) compared with polycrystalline Al, suggesting these materials have excellent resistance to corrosion damage caused by the growth of micrometer scale pits. However, synthesis of Al-based metallic glass coatings still remains a challenge.

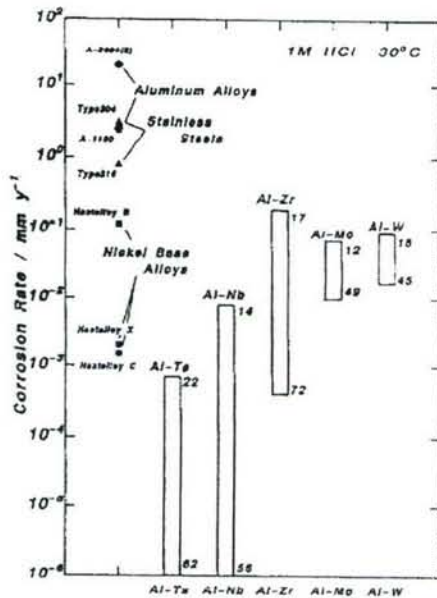


Figure 1. Corrosion rates of various aluminum alloys and conventional corrosion-resistant alloy measured in 1M HCl at 30°C

The following aluminum based bulk metallic glass coating materials were selected for this study.

- (i) Al-5Fe-5Gd (atom %)
- (ii) Al-8Ni-5Y (atom %)

Gas atomized spray powders under the trade name 'Flomaster<sup>TM</sup>' were obtained from F.J. Brodmann & Co. LLC. Elemental powders mixed in the desired proportions were tribochemically alloyed under Argon atmosphere to obtain these spray powders.

## II.2. Spray coating methods

### II.2.1 Cold Spray

Cold spray is a relatively new coating process developed in the mid-1980 at the Institute of Theoretical and Applied Mechanics of the Siberian Division of the Russian Academy

of Science in Novosibirsk. High-pressure carrier gas ( $\sim 3.5$  MPa or 500 psi) is required to impart high kinetic energy to the powder particles and to achieve supersonic velocities ( $\sim 500$ -1200 m/s). After the powder particles are accelerated to these high velocities, they impact the substrate causing the thin surface oxide layers to rupture, plastically deform at surface, come in close proximity of clean surfaces, thereby reconsolidating the particles bonding them together. A high degree of plastic deformation occurs at the surface regions due to the impact of the accelerated particles onto the substrate. The source of bonding is the kinetic energy achieved by the particles under high pressure accelerating gas, to impinge onto the substrate at temperatures ranging much below the melting point of the spray particles. The bonding in particles in this process is attributed to the adiabatic shear instabilities at the particle-substrate or particle-particle interfaces, caused by the heavy particle impact. The high velocity is developed by compressed gas flow (usually helium, nitrogen or their mixture) through high inlet pressure in a converging-diverging de Laval type of nozzle. Therefore, velocity of particles, attained prior to impact, holds a very important place in cold spraying. Brittle spray materials such as ceramics do not undergo required plastic deformation to form a good bond with the substrate; thereby, the solution to the problem above becomes use of ductile matrix or filler materials. Hence, the cold spray process is ideally suited for synthesizing pure metallic coatings. Since cold spray involves temperatures much lower than the melting points of spray particles, the coating experiences little or no phase changes during deposition. Since the cold spray is a solid-state process, grain growth and phase transformations are not expected during the cold spraying. Still, no microstructural evidence has been reported dictating the melting of the spray particle. Moreover, unwanted effects like oxidation, nitriding, decarburizing and any decomposition are also avoided in the process.

#### II.2.2. Plasma Spray

With the ability to deposit any material that melts since the plasma heat source is greater than 10,000K, coatings can be deposited on almost any substrate to a desired thickness. Powders are fed into the plasma where they get heated/melted and are accelerated toward the surface at supersonic speeds where they deposit and rapidly cool. The density of the plasma-formed material directly depends upon the plasma velocity (*kinetic energy*) and processing variables (*thermal energy*). Air plasma spray routinely produces high-density (90-95%) deposits. Plasma spray can deposit structures/coatings to a varied thickness from 100  $\mu\text{m}$  to a couple of inches with a dimensional tolerance of  $\sim 50$   $\mu\text{m}$ . Some of the advantages of the plasma spray process include:

- Thermal energy controllable from 10-80 kW
- Plasma gas and particle velocity variable from subsonic to supersonic speeds
- Compositional flexibility to spray a large variety of materials
- Rapid solidification ( $\sim 10^8$  K/sec) leading to refined or amorphous microstructure (*this property will be tapped to synthesize glassy and/or amorphous coatings of aluminum alloys*)
- Potentially lower cost of fabrication due to high yield

Fine powders of the crystalline coating materials were cold sprayed onto substrate coupons at ASB Industries, Barberton, Ohio. ASB Industries is collaborator of FIU under Dr. Arvind Agarwal.

The processing parameters of both plasma and cold spray methods were explored to synthesize crystalline and bulk metallic glass alloys based on Al.

### ***II.3. Microstructural characterization***

Microstructural characterization of coatings was performed making use of optical and SEM metallography, X-ray diffraction, and microhardness measurements.

### ***II.4. Tensile testing***

Tensile tests were performed on baseline and spray coated materials to assess their tensile properties.

### ***II.5. Corrosion testing***

#### ***II.5.1. Corrosion potential measurements***

Corrosion potential measurements were performed according to ASTM-G69 "Standard Practice for Measurement of Corrosion potentials of Aluminum Alloys." According to this procedure, the potentials are measured in sodium chloride/hydrogen peroxide electrolyte with a Saturated Calomel Electrode (SCE). The potentials are measured at different depths from the coated surface of the substrate coupon. For this purpose, the coupon thickness will be reduced to the desired level for each measurement by electrochemical machining making use of an electrolyte of saturated sodium chloride in water.

#### ***II.5.2. SWAAT Corrosion Test***

SWAAT tests were performed on coated substrate coupons according to ASTM-G85-A3 test procedure. This type of test involves a cyclic salt spray test that uses a 5% synthetic sea salt solution acidified to pH 3 with acetic acid in a spray chamber. Tests are performed by exposing the coated side of the coupons to SWAAT in order to assess their life.

## **III. RESULTS**

### ***III.1 Baseline results***

Baseline property data of bare and clad materials were generated at Touchstone for comparisons while assessing the performance of coated materials. These include mechanical properties, accelerated (SWAAT) corrosion tests and corrosion potentials.

The baseline data generated at Touchstone Research Laboratory are as follows (See Tables 1&2, and Figs. 2&3).

#### *III.1.1. Tensile results*

**TABLE 1. Baseline Tensile Results**

Alloy	Sheet Thickness (mm)	Y.S., MPa	UTS, MPa
2024-T3	0.6385	339.6	486.0
2024-T3 with clad	0.6413	334.7	451.9
7075-T6	0.8160	507.3	570.5
7075-T6 with clad	0.8090	482.7	540.5

#### *III.1.2. SWAAT results*

**TABLE 2. Baseline SWAAT Results**

Material ID	SWAAT life, hrs
2024-T3	828
2024-T3 with clad	1272+
7075-T6	342
7075-T6 with clad	1092

+ Test terminated without failure

#### *III.1.3. Corrosion Potentials*

In the clad materials, anodic layer can be noted from the following potential profiles.

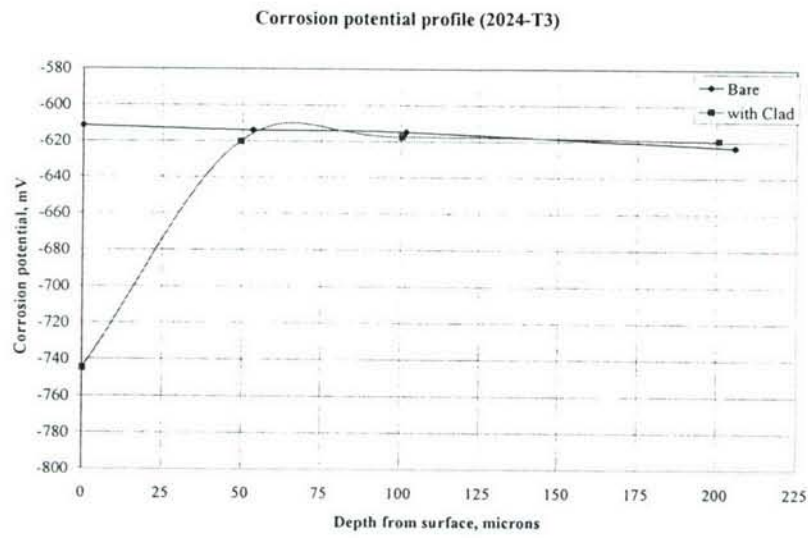


FIGURE 2

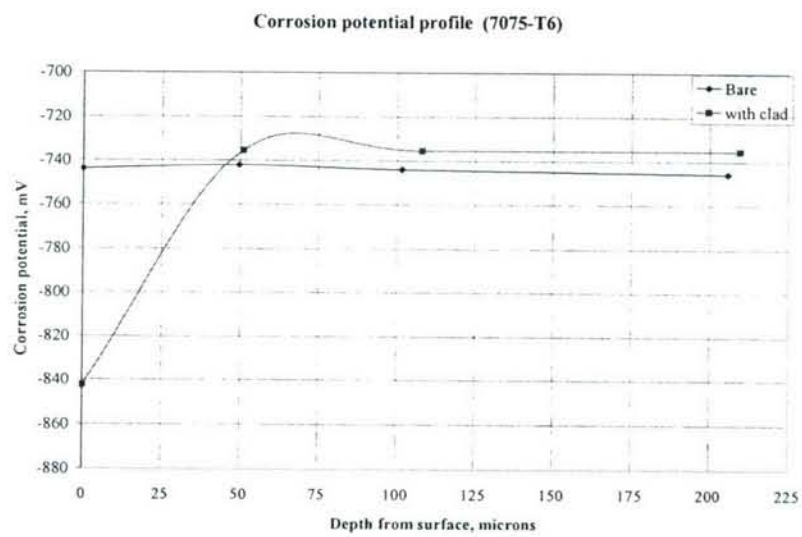


FIGURE 3

### III.2. Cold spray coatings

Cold spray processing of aluminum and aluminum-zinc composite coatings was done at ASB Industries, Barberton, Ohio. ASB used the H-20 aluminum powder, purchased from Valimet, as the spray feedstock for producing aluminum coatings on 2024-T3. ASB has already carried out extensive studies with this powder and have optimized the spray parameters to obtain dense and well bonded coatings. These parameters were used to produce the aluminum coated specimens. Unlike other thermal spray processes, cold spray process does not require pre-spray surface preparation by grit blasting operation.

Initially, 6061 aluminum plates were used as dummy substrates and the spray gun was operated with optimized parameters, given in the following Table 3.

**TABLE 3. Cold Spray Parameters**

#	Parameter	H-20 Al	Al-2%Zn
1	Gun Pressure	20 bar	20 bar
2	Gun Temperature	500 K	600 K
3	Main Gas and Flow Rate	Helium, 125 m <sup>3</sup> /Hr	Helium, 110 m <sup>3</sup> /Hr
4	Carrier Gas and Flow Rate	Nitrogen, 5 m <sup>3</sup> /Hr	Nitrogen, 5 m <sup>3</sup> /Hr
5	Powder feed rate	10 g/min	15 g/min

In order to produce Al-2%Zn composite feedstock, 490 g of aluminum and 10 g of zinc powders were blended in a Turbula blender, which uses a three dimensional blending motion to achieve homogenously blended material. About 200 g of zirconia balls was added to increase the blending efficiency. After 2 hours of blending, the charge was sieved off the zirconia balls to obtain composite spray feedstock.

Based on the previous results, a few spray experiments were carried out varying different spray parameters. Though a detailed spray experimental program will be needed to properly optimize all the spray variables, these small experiments could yield fairly optimized values, which yield acceptable coatings. 7075-T6 coupons were sprayed with parameters given in the above Table.

#### III.2.1. Characterization of cold Sprayed Al Coating (On 2024-T3 substrate)

**Coating Thickness :** 100-120  $\mu\text{m}$

**Microstructure:** As shown in Fig.4, these cold sprayed coatings are dense and adherent to the substrate. Some micropores / oxide stringers can be noted. These are typical characteristics in such coatings. Also, largely plastically deformed splat morphologies of these as-sprayed coating can be clearly seen from the high-magnification optical micrographs.

**Microhardness:** Variation along the coating thickness was in the range of HV 20-45 [See Fig. 5].

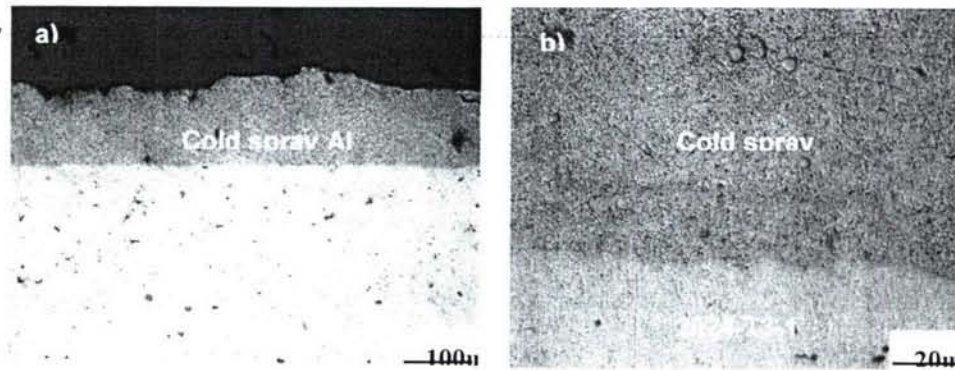


Figure 4. Cold sprayed Al coating microstructures at different magnifications

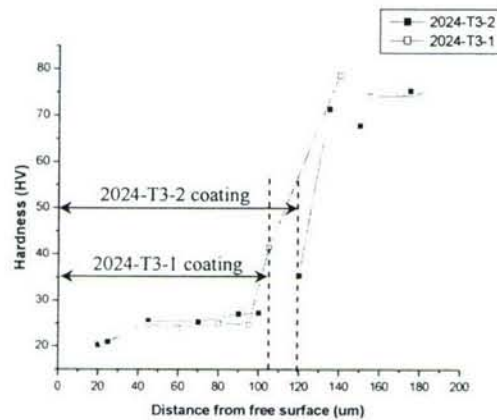


Figure 5. Hardness distribution along the coating thickness of cold sprayed Al coatings

### III.2.2 Characterization of cold sprayed Al-2 Zn Coating (On 7075-T6 substrate)

**Coating Thickness :** 90-115 μm

**Microstructure:** As shown in Fig.6, the cold sprayed coatings are dense and free of microcracks, but some pores can be found in these coatings. In comparison with cold sprayed Al coatings, these Al-Zn coatings seem to have slightly higher porosity. While coating is adherent to the substrate, there are signs of delamination in some samples suggesting desired improvement in substrate cleaning and preparation prior to the coating.

**Microhardness:** The microhardness variation in the Al-Zn coating is similar to Al coating [See Fig.7]. It implies that addition of zinc to aluminum in the coating has not caused much strengthening.

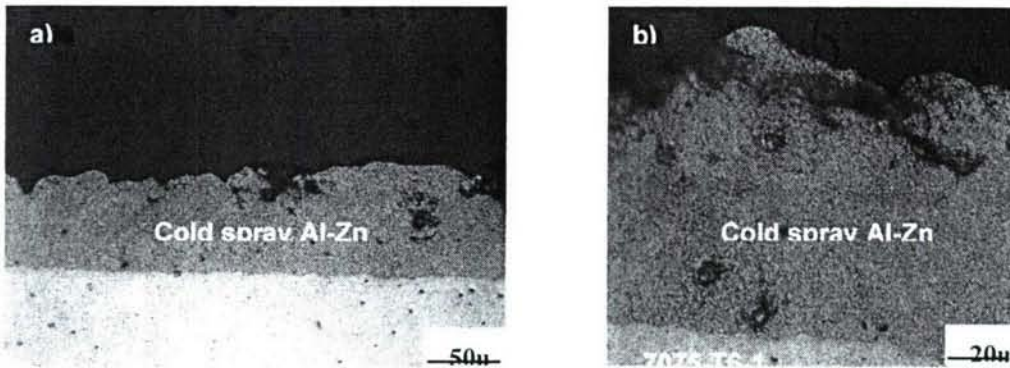


Figure 6. Cold sprayed Al-Zn coating microstructures at different magnifications

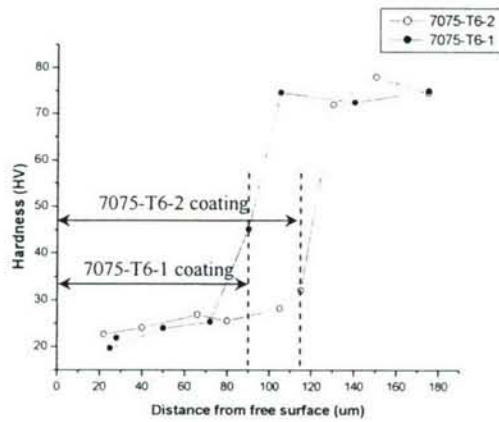


Figure 7. Hardness distribution along the coating thickness of cold sprayed Al-Zn coatings

### III.2.3. Tensile properties

Some softening is noted in cold spray coated materials. Tensile property changes in coated materials are summarized in Table 4.

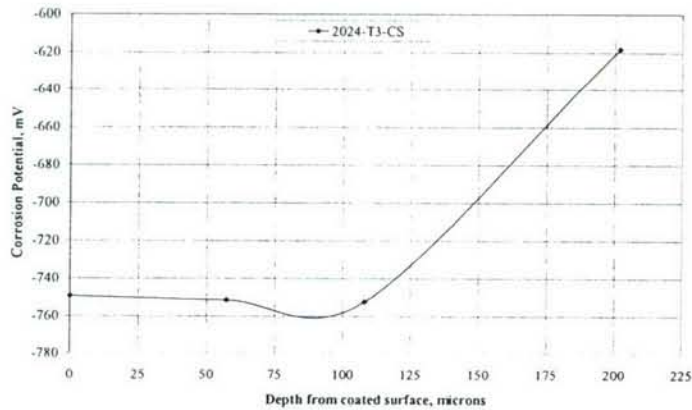
**TABLE 4. Tensile properties of cold spray (CS) coated and uncoated materials**

Material	Y.S., MPa	U.T.S., MPa
2024-T3-CS (Al)	281.4 (16% softening)	355.5 (20% softening)
2024-T3 (uncoated)	334.7	451.9
7075-T6-CS (Al-2 Zn)	450.9 (7% softening)	511.5 (5% softening)
7075-T6 (uncoated)	482.7	540.5

#### III.2.4. Corrosion potentials

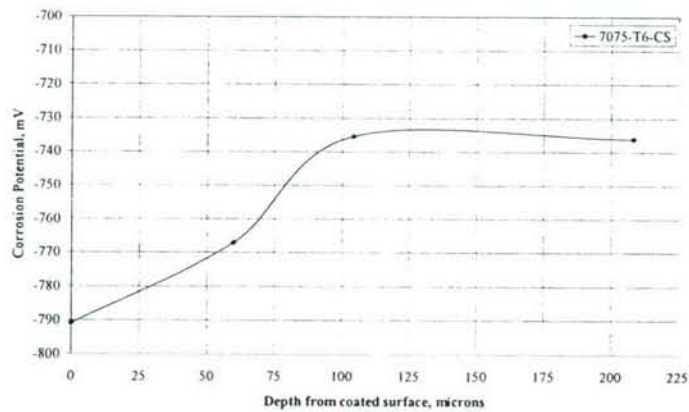
Corrosion potential profile of cold spray coated materials indicates an anodic layer at the surface with a drop in potential (Fig. 8 & 9).

**Corrosion Potential Profile of 2024-T3-Cold Sprayed (CS) (Al)**



**FIGURE 8**

**Corrosion Potential Profile of 7075-T6-Cold Sprayed (CS) (Al-2 Zn)**



**FIGURE 9.**

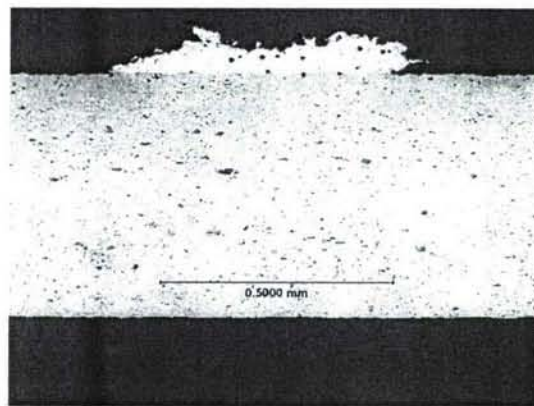
### III.2.5. SWAAT

**TABLE 5. SWAAT results of cold spray (CS) coated materials**

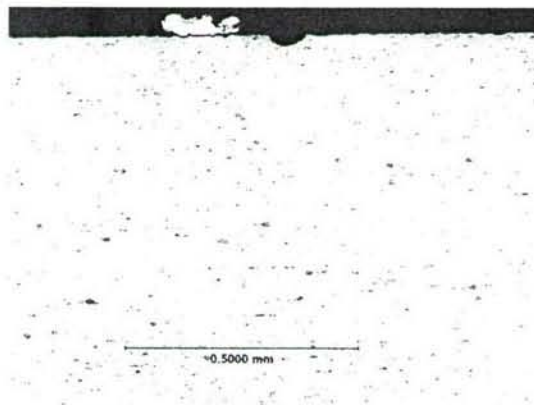
Material	SWAAT life in hrs
2024-T3 with Al coating	1272+
7075-T6 with Al-Zn coating	1272+

+ Test terminated without failure

While SWAAT results are shown in Table 5 for the cold spray coated samples, their corrosion damage is illustrated in Fig. 10.



(a) 2024-T3 with Al coating



(b) 7075-T6 with Al-Zn coating

**FIGURE 10. Cold spray coated samples exposed to SWAAT (1272 hrs)**

From this study, cold spray coating method is promising towards deposition of crystalline materials (Al on 2024-T3 and Al-Zn on 7075-T6). The cold spray coatings appear to be similar to the original claddings in their performance towards galvanic protection as indicated by their corrosion potentials and SWAAT life. The method is well suited for depot application of cladding materials.

There is, however, the issue of some strength loss as a result of coating application in cold spray process. While the softening is only 5-7 % in 7075-T6, it is up to 20 % in 2024-T3. Further work should address this issue to eliminate softening of the substrate.

### ***III.3. Plasma spray coatings***

#### ***III.3.1. Crystalline coatings***

##### **III.3.1(a). Plasma Sprayed Al Coating on Al 2024-T3 substrates**

Plasma spraying conditions were optimized in order to get a coating without warping the substrate and keep substrate temperature less than 150°C. Following plasma spraying parameters were carried out:

1) Primary gas:	40psi
Career gas:	30psi
Secondary gas :	90psi
Substrate to gun distance:	4in
Plasma Power :	600A x 40V
Feed Rate:	3RPM
Substrate was secured by clamping at both ends	

**Results:** Coating was good. Maximum substrate temperature was around 120°C. The substrate was warped on cooling and it was like a flat bell shape.



Figure 11. Plasma sprayed coupon (Al on 2024-T3): (a) warped & (b) relatively less deformed

2) Primary gas: 40psi  
 Carrier gas: 30psi  
 Secondary gas : 90psi  
 Substrate to gun distance: 5in  
 Plasma Power : 400A x 40V  
 Feed Rate: 2.5RPM  
 Substrate was secured by clamping at on end

**Results:** Maximum substrate temperature was 89°C. The substrate was deformed to a lesser degree this time, as shown in Fig. 11b. Clamping at one end does not lead to thermal stresses on cooling. 15 samples were sprayed with these conditions. The thickness of the coating is about 50-60 µm. These samples were analyzed for corrosion and mechanical properties.

Also, the change in substrate's temperature with spraying time is clearly indicated in Figure 12. Substrate temperature during plasma spraying was recorded using an optical pyrometer by an incident laser beam on the back side of the substrate.

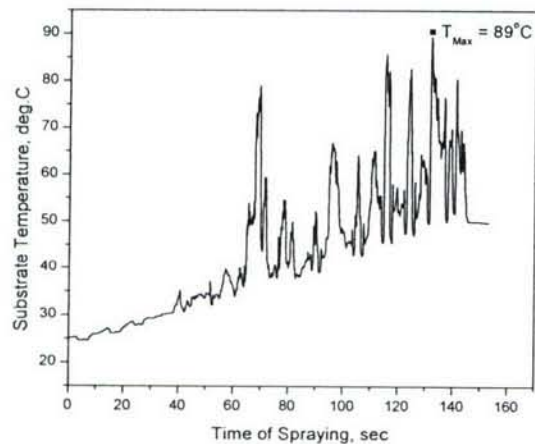


Figure 12. Change in temperature of the substrate along with the spraying time (Al coating)

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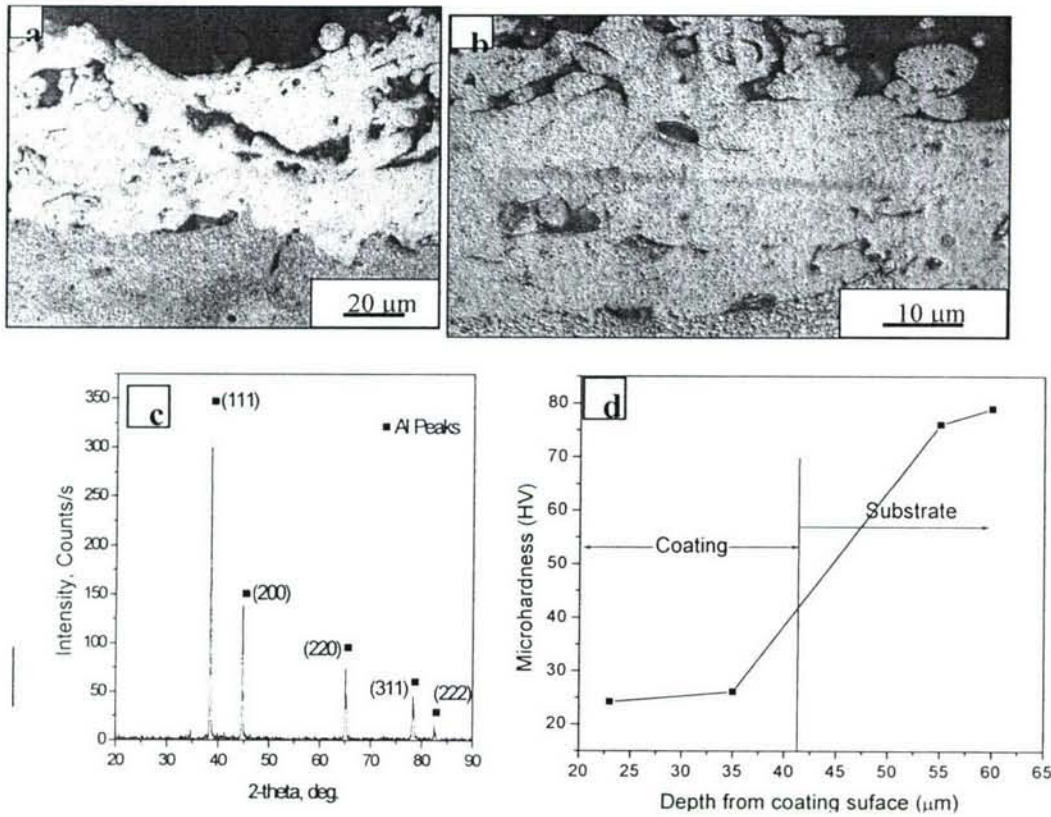


Figure 13. a) Low magnification optical micrograph of coating, b) High magnification optical micrograph of coating, c) XRD pattern of the coating, and d) Hardness profile along the depth of the coating

Comments:

- The interface is good and interlocking of the coating and substrate can be seen.
- The coating shows presence of small amount of porosity which is typical of plasma sprayed coatings.
- XRD shows peaks of aluminum and absence of oxides.
- Microhardness of the coating varied between HV 25-42 similar to cold sprayed coating.

### III.3.1(b). Plasma Sprayed Al-Zn Coating on Al 7075-T6 substrates

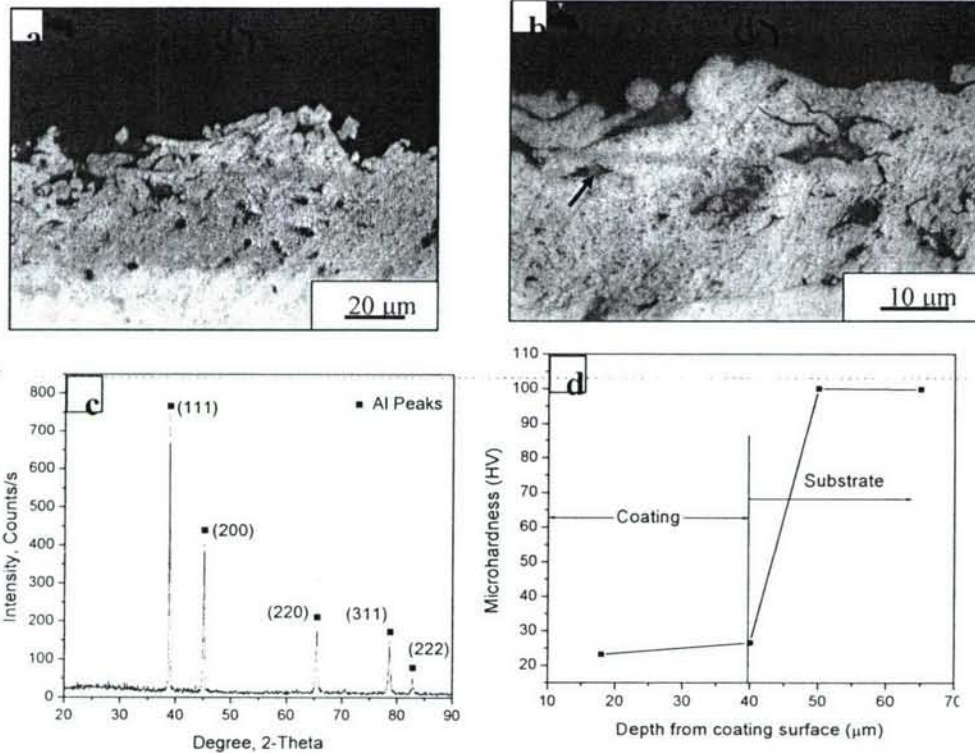


Figure 14 a) Low magnification optical micrograph of coating, b) High magnification optical micrograph of coating, c) XRD pattern of the coating, and d) Hardness profile along the depth of the coating

#### Comments:

- The interface is good and interlocking of the coating and substrate can be seen.
- The coating has the typical splat like microstructure and shows presence of small amount of porosity. Some second phase is seen in the high magnification picture (marked by arrow) which might be zinc.
- XRD shows peaks of aluminum and absence of zinc and oxides. Probably zinc is in the form of solid solution in aluminum. Some free zinc is present but its fraction is low to be detected by XRD.
- Hardness is similar to plasma sprayed 1100Al coatings.

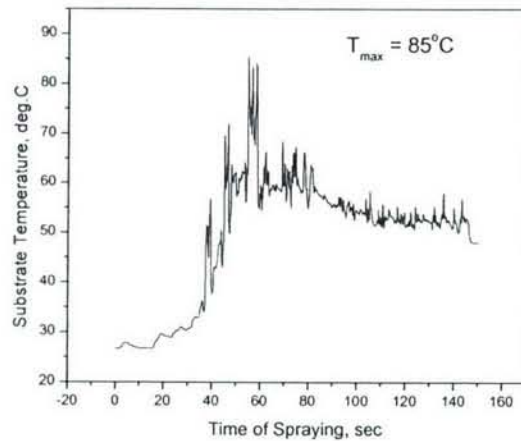


Figure 15. Change in substrate temperature with spraying time

### III.3.1(c). Tensile properties and corrosion test results (Crystalline coatings)

Tensile property changes in coated materials are summarized in Table 6. Softening up to 22% in strength, especially in 2024-T3, can be noted.

**TABLE 6. Tensile properties of plasma sprayed (PS) specimens (crystalline coatings)**

Material	Y.S., MPa	U.T.S., MPa
2024-T3 (PS)	260.3 (22% softening)	361.6 (20% softening)
2024-T3 (without coating)	334.7	451.9
7075-T6 (PS)	433.3 (15% softening)	506.3 (11% softening)
7075-T6 (without coating)	507.3	570.5

Corrosion potential profiles of cold spray coated materials with crystalline coatings indicate an anodic layer with a drop in potential of about 50-80 mV (Figs. 16 & 17).

Corrosion potential profile: Plasma sprayed Al coating on 2024-T3

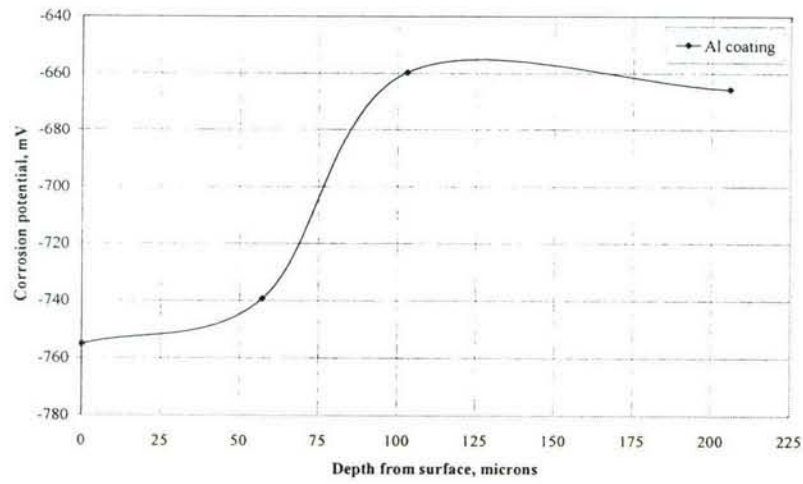


FIGURE 16

Corrosion potential profile: Plasma sprayed Al-Zn coating on 7075-T6

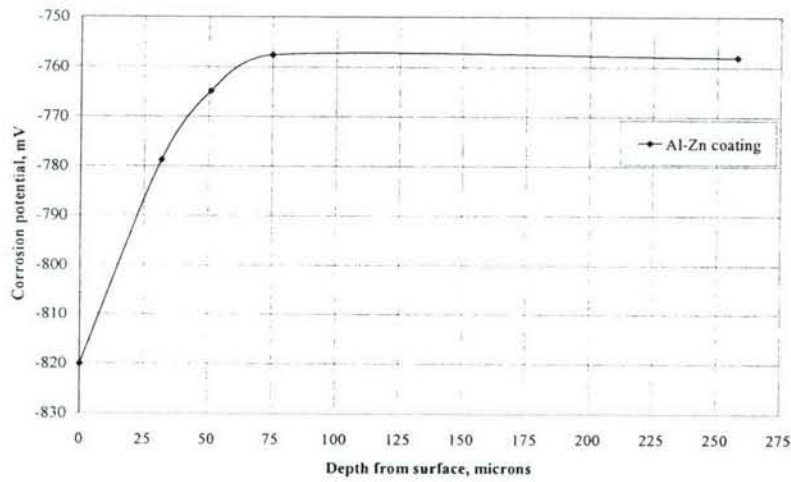


FIGURE 17

**TABLE 7. SWAAT data of samples with plasma spray coated crystalline coatings**

Material	SWAAT life in hrs
2024-T3 with Al coating	1272+
7075-T6 with Al-Zn coating	1218+

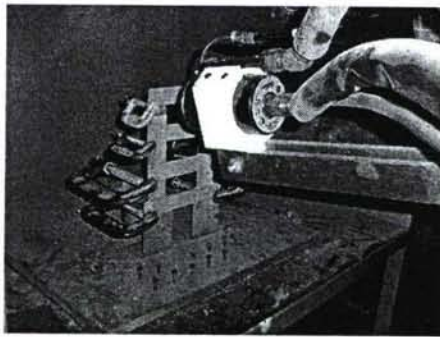
+ Test terminated without failure

The overall results of plasma sprayed specimens with crystalline coatings are similar to those with cold sprayed crystalline coatings. Galvanic protection can be restored through the application of these crystalline coatings. Even though the recorded temperatures of specimens during plasma spraying are below 100<sup>0</sup>C, some softening seems to occur.

#### ***III.4. Al based Bulk Metallic Glassy Coatings by Plasma Spray Technique***

Plasma spray experiments were performed to produce the Al base metallic glassy coating from metallic powder Al-5Fe-5Gd and Al-8Ni-5Y. The coating thickness obtained for both of the coating is 100 $\mu$ m. The microstructural development and the phase determination are investigated by the combination of optical metallography and X-ray diffraction. Hardness of the coating is measured by the Vickers microhardness tester. Change in temperature of the substrate along with the spraying time is recorded for both of the coatings.

**Figure 18** shows the experimental setup of plasma spray coating of Al-based metallic glassy powder on 7075-T6 substrate.



**Figure 18.** Plasma spraying coating of Al-based metallic glassy powder

#### III.4.1. Characterization of Al-5Fe-5Gd

Topographical features of Al-5Fe-5Gd coated sample is shown in **Figure 19**. The coating is approximately 150  $\mu\text{m}$  thick and has low porosity. Two phase microstructure is seen from **Figure 19(b)** with second phase in between the splats of Al. X-ray diffraction (XRD) spectrum is presented in **Figure 20** which shows presence of Al and Fe peaks. Gd seems to have gone into solution. Lower degree of mixing is observed due to rapid solidification conditions. Hardness distribution of plasma sprayed Al-5Fe-5Gd coating is shown in **Figure 21**, which indicates that the hardness of the substrate is higher than the coating.

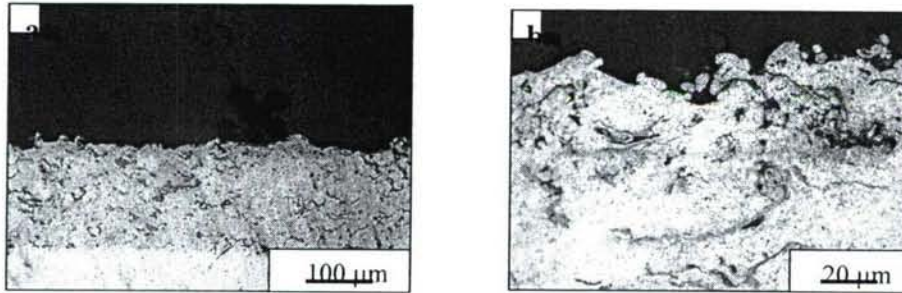


Figure 19. Plasma Sprayed Al-5Fe-5Gd Coating on 7075-T6 Substrate at (a) low and (b) high magnification

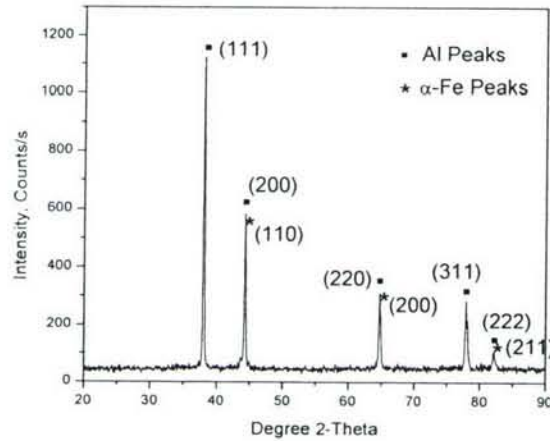


Figure 20. XRD of plasma sprayed Al-5Fe-5Gd coating

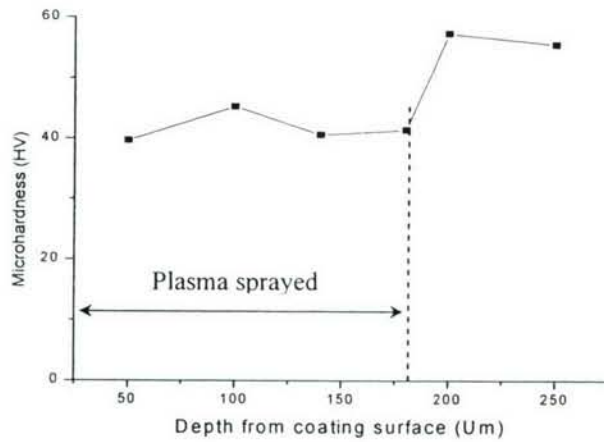


Figure 21. Hardness distribution of plasma sprayed Al-5Fe-5Gd coating

**Figure 22** shows the change in the substrate temperature along with the spraying time. The maximum substrate temperature is recorded  $133^{\circ}\text{C}$ . This temperature is significantly higher than  $89^{\circ}\text{C}$  which was observed for spraying Al and Al-Zn coating. This could lead to softening of the substrate. Though temperature ( $133^{\circ}\text{C}$ ) is lower than critical limit of  $150^{\circ}\text{C}$ , it appears to be sufficient to cause softening.

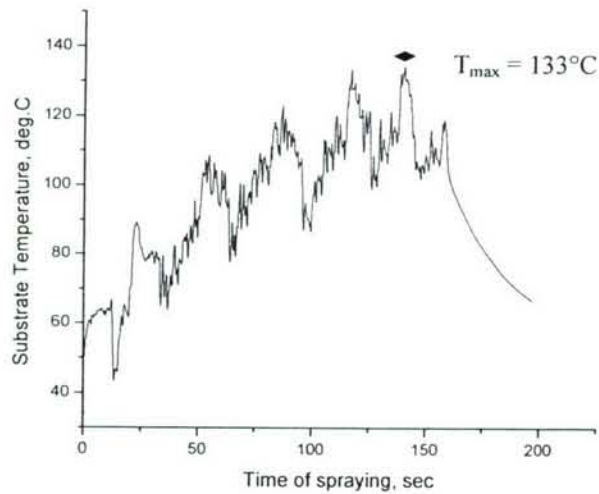


Figure 22. Change in temperature of the substrate along with the spraying time

#### III.4.2. Characterization of Al-8Ni-5Y

Topographical features of Al-8Ni-5Y coated sample is shown in **Figure 23**. The coating is approximately 350  $\mu\text{m}$  thick and has low porosity. From figure 6b we can see that there are three distinct phases. This also shows limited alloying in the coatings. X-ray diffraction spectrum is presented in **Figure 24** that shows Al and Ni peaks. Y peaks are not observed. Hardness distribution of plasma sprayed Al-8Ni-5Y coating is shown in **Figure 25**. Hardness of the plasma sprayed Al-8Ni-5Y coating is found to be uniform throughout the coating thickness. **Figure 26** shows the change in substrate temperature along with the spraying time. The maximum substrate temperature is recorded 124°C which also caused softening of the substrate.

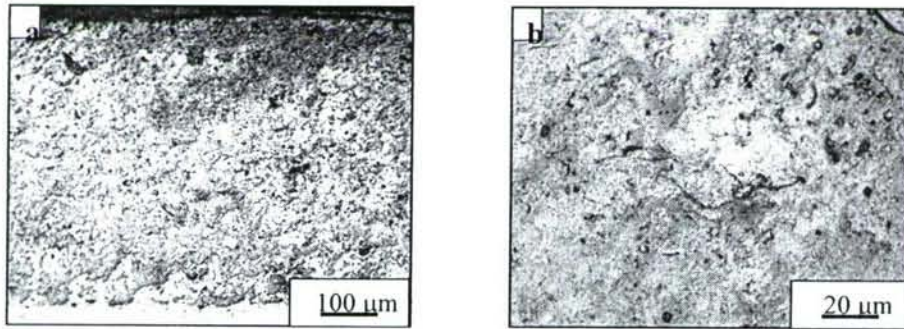


Figure 23. Plasma Sprayed Al-8Ni-5Y Coating on 7075-T6 Substrate (a) at low and (b) high magnification

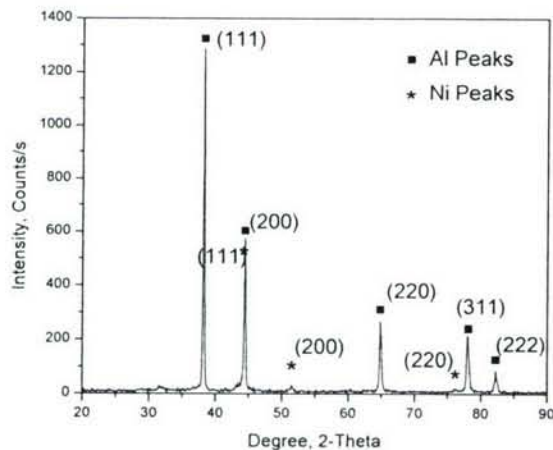


Figure 24. XRD of plasma sprayed Al-8Ni-5Y coating

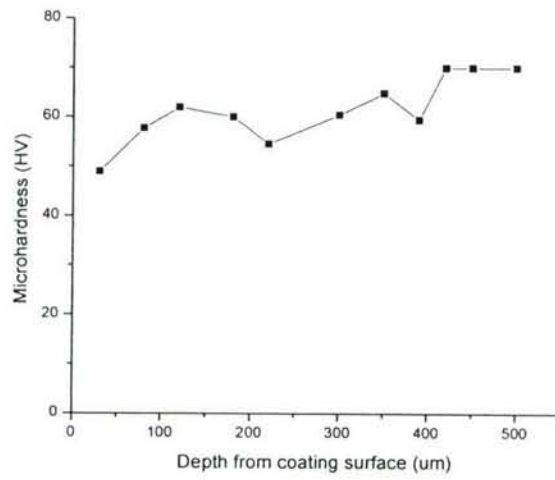


Figure 25. Hardness distribution of plasma sprayed Al-8Ni-5Y coating

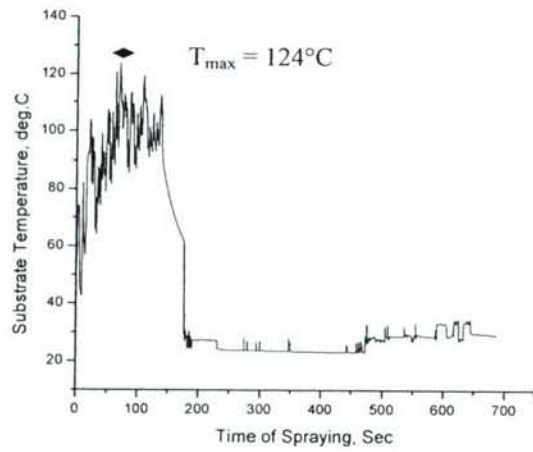
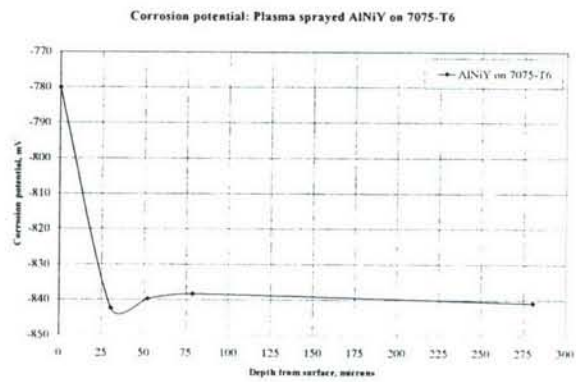


Figure 26. Change in temperature of the substrate along with the spraying time (Al-8Ni-5Y)

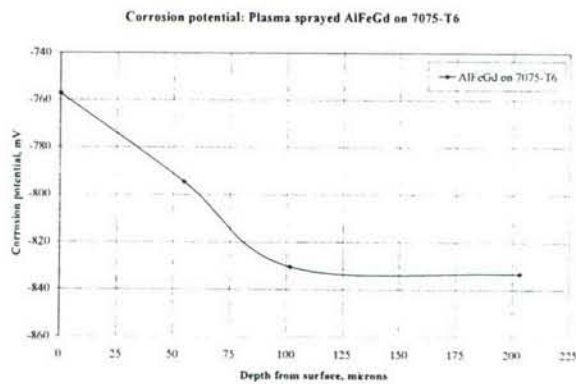
### III.4.3. Tensile properties and corrosion test results (BMG coatings)

**TABLE 8. Tensile properties of plasma sprayed (PS) specimens (BMG coatings)**

Material	Y.S.,MPa	UTS, MPa
7075-T6 (without coating)	507.3	570.5
7075-T6 (PS) with Al-Ni-Y coating	189.9 (63% softening)	344.2 (40% softening)
7075-T6 (PS) with Al-Fe-Gd coating	160.1 (68% softening)	303.2 (47% softening)



**FIGURE 27**

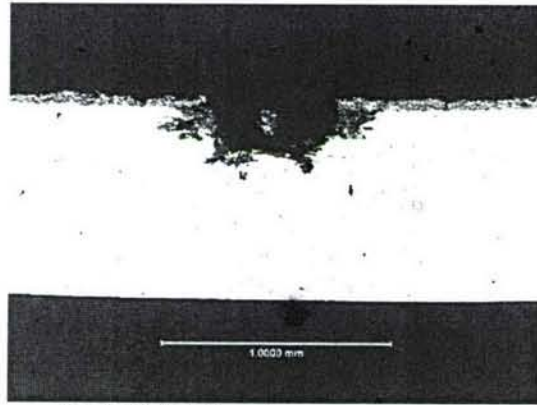


**FIGURE 28**

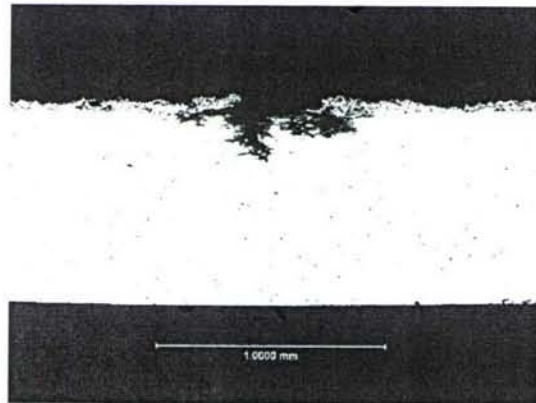
**TABLE 9. SWAAT data of samples with plasma spray coated BMG**

Material	SWAAT life in hrs
7075-T6 with Al-Ni-Y coating	208
7075-T6 with Al-Fe-Gd coating	252

+ Test terminated without failure



(a) Al-8Ni-5Y coating



(c) Al-5Fe-5Gd coating

**FIGURE 29. SWAAT Corrosion Damage In 7075-T6 with BMG Coatings**

### III.5. Comments

Plasma spray trials of BMG (Al-8Ni-5Y and Al-5Fe-5Gd) coatings did not yield glassy phases. The lack of availability of Al-based BMG powder feedstock is a major shortcoming in this regard.

Samples with BMG trial coatings exhibited a higher amount of softening than others (See Table 8). The observed temperature of the substrate in the BMG coating trials is also higher than in other specimens of this study. Plasma spray parameters should be further optimized to obtain lower substrate temperature to avoid softening of the substrate. This could be achieved by (i) external cooling of substrate and (ii) thermal modeling.

Corrosion potential plots shown in Figs. 27 and 28 indicate a cathodic surface layer relative to the substrate with both BMG coatings. Obviously, galvanic protection is not possible with these coatings. If any pores and microcracks are present in the coating, they will progress quickly as a pit into the substrate. This leads to lower corrosion resistance as seen from their poor SWAAT life. The SWAAT corrosion damage of localized pitting type can be seen in Fig. 29.

If Al based bulk metallic glass coatings are developed, they may provide barrier protection against corrosion.

## IV. ESTIMATES OF TECHNICAL FEASIBILITY

### IV.1. Conclusions

Phase I research has resulted in the following conclusions:

- Aluminum and Aluminum-Zinc materials were successfully deposited as crystalline coatings on 2024-T3 and 7075-T6 substrates by both, plasma spray and cold spray techniques.
- An attempt was made to synthesize Al-8Ni-5Y and Al-5Fe-5Gd (atom %) based glassy coatings by plasma spray technique. Segregation of alloying elements leads to lack of formation of glassy phase. Lack of availability of prealloyed glassy powder feedstock in the desired composition was a major hurdle.
- Maximum substrate temperature during plasma spraying varied between was 89-135°C for different coatings. This was much lower than critical requirement of temperature lower than 150°C for aircraft skin. Despite the lower temperature of the substrate while coating, a drop in tensile strength occurred in some of the coupons. Cumulative aging of the substrate alloy during the coating deposition appears to give rise to the age softening.
- Corrosion tests (SWAAT and corrosion potential measurements) were performed on materials with crystalline coatings. The corrosion resistance of the coated materials (crystalline) was similar to the original alclad materials. Corrosion properties of Al-Ni-Y and Al-Fe-Gd based glassy coatings were poor due to

segregation of alloying elements which formed several galvanic cells in the coating leading to pitting and accelerated corrosion.

Based on the above conclusions, following estimates of technical feasibility can be made.

#### ***IV.2. Technical Feasibility of Coating Process***

1. Both coating processes are effective to synthesize coating in an economic manner as they can deposit coatings on large and complex structures in a short period.
2. The availability of cold spray portable machine makes it very attractive process for on-site coating deposition and coating repair.
3. Both processes need to be optimized to avoid substrate softening. This can be achieved by heat transfer modeling of the coating/substrate system.

#### ***IV.3. Technical Feasibility of Coating Material***

1. Conventional crystalline coatings (Al and Al-Zn) displayed similar corrosion properties as original alclad materials.
2. Researchers have shown that aluminum based glassy phase has improved corrosion resistance. However, those studies have been performed on cast glassy alloys. Synthesis of Al based glassy coating by any process is still unfound in the literature. Our study proves that it is feasible to deposit Al based glassy coatings if prealloyed glassy powder can be obtained. Lack of prealloyed aluminum based glassy powder is the major impediment in development of these coatings. Discussion with a major aluminum alloy powder vendor suggested that such an effort requires major research expenditure to develop Al based glassy powder. We strongly feel that vacuum plasma alloying of blended powder could result in formation of Al based glassy powder with a modest expenditure.

#### ***IV.4. Overall Estimate of Technical Feasibility***

Aluminum based metallic glass is an excellent candidate for corrosion protection. Both plasma spray and cold spray processes can be utilized to deposit these coatings on large and complex structures. The key requirement is to synthesize prealloyed metallic glass powder.

#### **Appendix: Cumulative list of people involved**

**At Touchstone:** Dr. G.S. Murty (PI)

**At FIU, Miami, FL:** Dr. Arvind Agarwal (PI)